Review

Platinum oxide formation and reduction during NO oxidation on a diesel oxidation catalyst – Experimental results

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ABSTRACT

Experimental investigations clearly show that the activity of a diesel oxidation catalyst (DOC, Pt-γ-Al$_2$O$_3$) is changing during NO oxidation. This can be attributed to the reversible formation of platinum oxide. Therefore the activity depends strongly on the pretreatment and the operating conditions. In this paper, the impact of O$_2$ and NO$_2$ as oxidising agents and of NO as reductant for platinum as well as the influence of different pretreatments is experimentally studied under typical DOC conditions in an isothermal flat bed reactor with either constant temperature or with temperature ramps. Furthermore, a method to determine the platinum oxide fraction in situ is shown.

An inverse hysteresis in NO conversion is observed if the temperature is linearly increased and subsequently decreased at constant gas composition, confirming the findings of Hauptmann et al. [1]. A variation of the minimal temperature of the ramp shows that a reduction of PtO by NO is possible in a net oxidising atmosphere (500 ppm NO, 12% O$_2$, 10% H$_2$O) below 220 °C. Above 300 °C, PtO becomes instable. Experiments with and without NO$_2$ prove that small NO$_2$ concentrations (<200 ppm) have no influence on the progress of platinum oxidation in the presence of 12% O$_2$. Platinum oxidation is mainly driven by the high O$_2$ concentration, which is confirmed by an observed deactivation of CO oxidation after reductive pretreatment. In a mixture of CO and NO, the light-off and light-out behaviour of both components is strongly modified by the other component.

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1. Introduction

The diesel oxidation catalyst (DOC) was originally developed as a stand-alone device to oxidise CO and unburned hydrocarbons in the exhaust gas. Nowadays, the DOC is in most applications combined with a diesel particulate filter (DPF) and either a NO_x storage catalyst (NSCs) or a selective catalytic reduction (SCR) catalyst. Typically, the DOC is positioned upstream of the other units in order to increase the NO_2/NO_x ratio [2]. A higher ratio increases the low temperature soot oxidation rate of DPF and the NO_x conversion efficiency of SCR and NSC. A correct prediction of the DOC's NO conversion is crucial for the simulation of the whole aftertreatment system.

So far, the DOC activity is usually assumed to be a constant value in macrokinetic models. But deactivation effects during NO oxidation have been reported in literature several times [3–5]. Olsson and Fridell [6] observed a decline in NO conversion from 76 to 25% on a Pt/Al_2O_3-DOC with 110 gPt/ft^3 at 300 °C within three hours. For a Pt/Al_2O_3-DOC with 80 gPt/ft^3, Hauptmann et al. [1] measured a loss from 95 to 80% NO conversion within 14 h at 169 °C. Smeltz et al. [7] found that the order in which NO and NO_2 is dosed in the feed influenced the catalyst performance. Starting with NO_2 reduces the activity by 25–50% compared to experiments starting with NO. If the catalyst is purged with NO, the activity is recovered. Due to the proceeding deactivation, the NO oxidation hardly ever reaches a stationary state [8].

This behaviour can be attributed to the formation of platinum oxide, which is less active for the oxidation of NO compared to platinum [9]. The formation of platinum oxide is induced not only by O_2, but also by NO_2, which is able to generate a higher oxygen surface coverage than O_2 due to its coordinative flexibility [10–12]. For $Pt(1 1 1)$ and $Pt(1 0 0)$ it was observed, that the oxidation starts with chemisorption of oxygen atoms at the Pt surface. Then surface oxide domains are formed where oxygen atoms adsorb on top of the surface oxide. Finally, bulk-like Pt-oxide particles grow [13], by which the platinum surface is disordered [14]. According to Wang and Yeh [15], oxygen adsorbs at ambient temperature. Above 27 °C, the platinum surface is reconstructed for extensive accommodation of oxygen. Around 470 °C, a stable surface layer of platinum oxides is formed. Above 530 °C, oxygen and/or platinum dioxide is desorbed. Hwang and Yeh [16] specified the temperature range for PtO and PtO_2 formation: Surface platinum oxide is formed above 25 °C. PtO appears above 100 °C whereas PtO_2 is formed above 300 °C. Above 600 °C, platinum reacts with Al_2O_3 to $PtAl_2O_4$. Wang and Yeh [17] measured the oxygen uptake by TG-DSC for Rh/Al_2O_3, Pd/Al_2O_3 and Pt/Al_2O_3 catalysts. Above 300 K, Rh/Al_2O_3 and Pd/Al_2O_3 have a high oxygen uptake, indicating the formation of bulk oxides. On the contrary, the oxygen uptake of Pt/Al_2O_3 is significantly lower, which could be explained by the formation of a protective surface oxide layer, which prevents the diffusion of oxygen into the bulk of the platinum.

The formation of platinum oxides was detected by Olsson and Fridell et al. [6,18] through XPS analysis for a $Pt/BaO/Al_2O_3$-NSC and a Pt/Al_2O_3-DOC. After reducing pretreatment, the spectrum of pure platinum was measured. Oxidising pretreatment with NO_2 resulted in overlapping spectras of Pt, PtO and PtO_2.

It is assumed that smaller particles form oxides more easily [18]. Pt clusters have a stronger tendency to form oxides than the bulk metal [19]. Furthermore, additives in the washcoat formulation influence the platinum oxide formation [4,20]. Acidic additives hinder the platinum oxide formation, whereas basic additives advance it. Furthermore, the activity of platinum towards NO oxidation is strongly influenced by the support and washcoat material [21]. The NO oxidation on Pt/SiO_2 is more active than on Pt/Al_2O_3, because platinum on SiO_2 is not so easily oxidised [22]. The stability of platinum oxide is increased in the presence of alkaline earth metals (e.g. barium), which renders a decline of the NSC's oxidation activity [18].

The deactivation is reversible, as the platinum oxide can be regenerated thermally above 400 °C in UHV [23] and above 650 °C at ambient pressure [22]. Alternatively, platinum oxide can be reduced at lower temperatures by NH_3 or NO [22]. The activity of PtO_2 is lower than for Pt because the binding ability of oxide towards O, O_2 and NO is weaker and the reaction barriers change [24,22].

The reason for our studies on platinum oxidation was the observed difference in NO oxidation activity of a NSC between stationary and dynamic conditions [25]. The NO reaction rate during lean rich cycling under almost stationary conditions, i.e. at the end of the lean phase, turned out to be higher (factor 3.5) than in lean stationary experiments. This effect might be attributed to the reduction of platinum oxide during the rich phase, which caused a higher activity in the following lean phase. Another reason was a study on thermal aging of DOCs, which showed that the reaction rate of CO and propene oxidation correlates linearly with the catalytically active surface [26]. For the NO oxidation, this correlation did not work, which might be due to the fact that the NO oxidation is structure sensitive or it is influenced by platinum oxidation. Smeltz et al. [7] proved by a study of $Pt(1 1 1)$ and $Pt(3 2 1)$ single crystals that the intrinsic rate for NO oxidation is not structure sensitive. The observed increase of activity with particle size is rather caused by the fact that small platinum particles are easier oxidised whereas larger particles are only partially oxidised and therefore more active.

In this work, different experiments with constant temperature and temperature ramps have been accomplished to characterize the conditions for formation and decomposition of platinum oxide. The experiments were carried out in an isothermal reactor to avoid axial and radial temperature gradients. We can confirm the very interesting findings of Hauptmann et al. [1], that an inverse hysteresis in NO conversion occurs if the temperature is linearly increased and subsequently decreased under constant gas atmosphere. Due to the here used isothermal setup, it can be excluded that the observed hysteresis is caused by temperature differences. To elucidate the conditions of platinum oxide formation, the minimal and maximal temperature of the ramp is varied, cooling down is run in different gas atmospheres and a holding time at the minimal temperature is introduced. This shows that platinum oxidation by O_2 is in competition with reduction of platinum oxide by NO. It depends on the gas composition and the temperature which one prevails. At high temperatures, platinum oxide decays thermally.

2. Experimental

A near-series model catalyst (Pt-γ-Al_2O_3, 130.06 g/ft^3, 400 cpsi monolith) from a commercial catalyst supplier was used for the experimental investigations. The catalyst was hydrothermally pretreated for 16 h at 700 °C with 10% water in air. The catalyst has a dispersion of 10.7 %, measured by CO-chemisorption [27]. The particle size analysis by HR-TEM showed that the particle size is between 15 and 250 nm with a mean particle size of 72 nm. The characterization of the catalyst is described more detailed by Boll et al. [27], where the catalyst is named DOC120.

After pretreatment, catalyst slices (30 mm × 40 mm × one channel high = 1.4 mm) were taken from the center of the monolith for kinetic measurements. They were carried out in an isothermal flat bed reactor (Fig. 1) under realistic flow conditions with synthetic exhaust gas and a space velocity of 40,000 1/h [25,26]. The reactor consists of a bottom and a top shell, made from stainless steel, and thermostated by heating cartridges. Five catalyst slices are placed in the groove of the bottom shell behind one
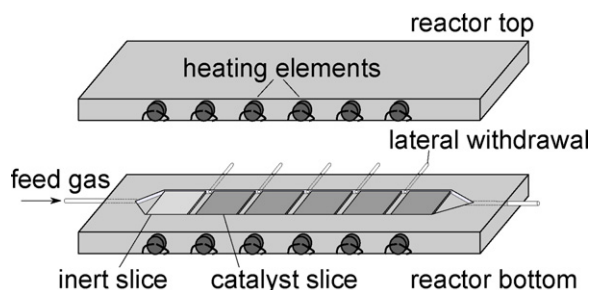
Fig. 1. Sketch of the isothermal flat bed reactor.

inert slice for gas preheating and uniform flow distribution. As the thin slices are surrounded by massive metal shells with high thermal mass, isothermal conditions can be maintained in the catalyst despite the heat release of exothermal reactions. A thermocouple is placed in the middle of each catalyst slice to measure the temperature. Lateral withdrawals after each slice allow the measurement of concentration profiles along the catalyst length. Gas analysis was accomplished with SI-mass spectroscopy (MS4) and FTIR (Multigas2030).

3. Results

3.1. Experiments with temperature ramp

3.1.1. NO temperature ramp

For measuring the platinum oxidation, experiments with a temperature ramp were undertaken under conditions quite similar to those of Hauptmann et al. [1]. At the beginning of the experiment, the catalyst was pretreated with 3% H_2 at 350 °C for 1800 s, see Fig. 2. Afterwards the catalyst is cooled down in inert atmosphere to the starting temperature of the ramp. Then the temperature is cycled between 150 and 400 °C with a linear ramp of 5 K/min. The feed consisted of 500 ppm NO, 12% O_2 and 10% H_2O in nitrogen.

The highest activity is observed for the first increasing temperature ramp directly after reducing pretreatment (1a, Fig. 3). This is caused by the fact that all platinum is present as metallic platinum at the beginning of the experiment. With increasing temperature, the platinum is progressively oxidised by O_2 and NO_2, the product of NO oxidation. Above 350 °C, the conversion of NO oxidation is decreasing due to thermodynamical limitation and gives therefore no indication if the catalyst deactivates further at higher temperatures. The ongoing in the high temperature range is studied further in Section 3.1.2.

The NO conversion during the subsequent cooling is significantly lower (1b, Fig. 3). This results in a hysteresis between light-off and light-out of NO oxidation. Contrary to the well known ignition/extinction hysteresis of CO oxidation, the light-out occurs at higher temperatures than the light-off (Fig. 3). Hauptmann et al. [1] refers to this effect as inverse hysteresis.

A second heating up followed directly after the first measurement (2a, Fig. 3). The conversion of NO oxidation is higher than during cooling down (1b). This reactivation at low temperatures
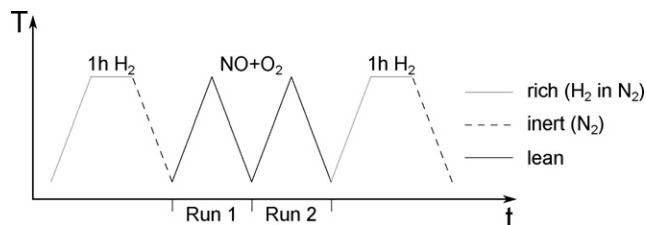

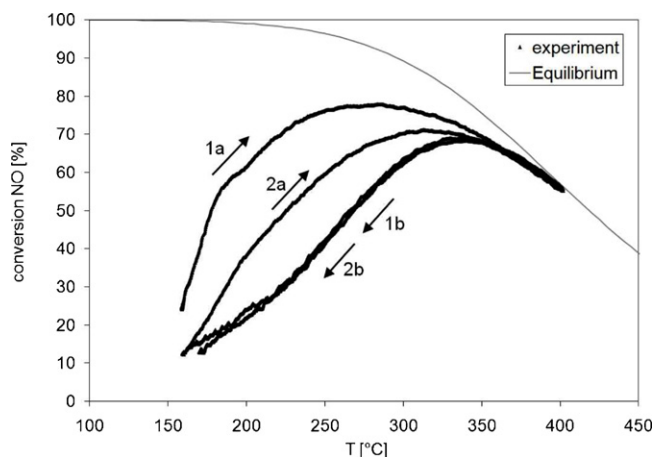**Fig. 2.** Scheme of the experiments with temperature ramp.

Fig. 3. First run (1) directly after reducing pretreatment with 3% H_2 and second run (2) of NO oxidation (500 ppm NO, 12% O_2, 10% H_2O) with linear temperature ramp (±5 K/min). (a) Heating, (b) cooling.

could be due to reduction of platinum oxides by NO at temperatures below 200 °C. The activity is only partly recovered as the conversion does not reach the level which it had after the reduction with H_2 (1a, Fig. 3). While re-cooling (2b, Fig. 3), the conversion is on the same branch like in the first measurement (1b, Fig. 3).

If the temperature is cycled between 250 and 350 °C, the hysteresis of NO conversion between heating and cooling disappears, compare Fig. 4. The conversion stays at the level of the deactivated branch, which means that under this gas composition no reactivation takes place above 250 °C. This comparison shows that it depends strongly on the operating conditions of the catalyst to which extent platinum oxidation and reduction influences the conversion behaviour.

3.1.2. NO temperature ramp with different atmospheres while cooling down

The atmosphere in which the catalyst was cooled down or pretreated before the experiment was varied in order to gain a better understanding of the platinum oxidation and reduction mechanisms. After the different pretreatments, the conversion behaviour was studied during ramps with rising temperature. The experiments Run 1 and 2 shown in Fig. 5 correspond to the experiments described in Section 3.1.1. Run 1 directly follows the pretreatment with 3% H_2. It can be assumed that at the beginning of the experiment platinum is not oxidised. The conversion at the beginning of Run 1 is therefore maximal. Run 2 follows after cooling down in the reaction gas mixture (500 ppm NO, 12% O_2 and 10% H_2O). In this case, platinum is already partially oxidised at the beginning of the temperature ramp, which therefore has a lower conversion. The experiments Run 3–5 are a variation of Run 2, where the cooling down was performed in another atmosphere than in the reaction gas mixture. Run 3 followed a cooling from 400 to 150 °C in nitrogen with 10% H_2O. Before Run 4, the catalyst was cooled down until 300 °C in the reaction gas mixture and then until 150 °C in nitrogen. For Run 5, nitrogen oxide was omitted while cooling down, but the atmosphere contained oxygen (12% O_2 and 10% H_2O in nitrogen).

Cooling in nitrogen implies that there is no reducing agent to reduce platinum oxide and no oxidizing agent to increase the amount of platinum oxide, so that the platinum content is frozen. To assure this, we cooled down in nitrogen from different temperatures and heated up to the same temperature and still found the same conversion. It can be seen from Run 3 in Fig. 5 that after cooling down in nitrogen from the maximum temperature (400 °C), the activity in the following NO oxidation is much higher than for Run 2 and is nearly as good as for Run 1, which followed directly
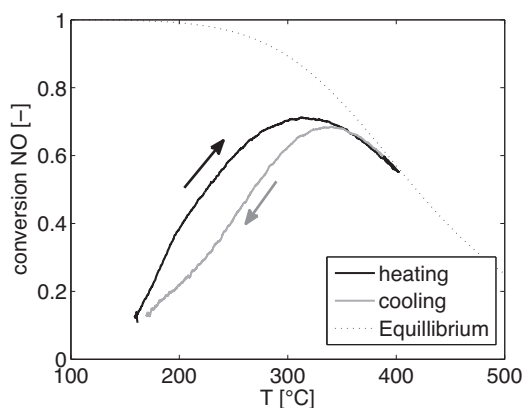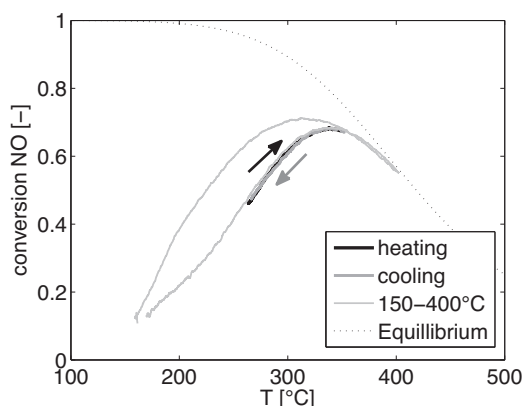
Fig. 4. Conversion of NO oxidation (500 ppm NO, 12% O_2, 10% H_2O) for a linear temperature ramp (± 5 K/min) with a starting temperature of (a) 150 °C respectively (b) 250 °C.

the pretreatment with H_2. This shows that platinum oxidation is not increasing further with higher temperatures above 350 °C. Due to thermal instability of platinum oxide there is less platinum oxide present at higher temperature. Run 4, which follows after cooling down in nitrogen from 300 °C to 150 °C, leads to a lower

Fig. 5. Conversion of NO oxidation (500 ppm NO, 12% O_2, 10% H_2O) after different pretreatments. Run 1: after pretreatment with 3% H_2. Run 2: after cooling down in reaction gas mixture. Run 3: after cooling down in nitrogen and 10% H_2O (<400 °C). Run 4: cooling down with reaction gas mixture until 300 °C, then further cooling to 150 °C in nitrogen and 10% H_2O. Run 5: cooling down in 12% O_2 and 10% H_2O.

conversion than Run 3. This indicates that at 300 °C more platinum oxide exists than at 400 °C. After cooling down with oxygen (Run 5) nearly the same activity is observed at the start of the rising temperature ramp as after cooling down in the reaction gas mixture (Run 2). Apparently, platinum oxide is formed to the same extent if there is only 12% O_2 present without NO_2. This will be studied further by isothermal experiments (compare Fig. 8). Above 200 °C, however the conversion surprisingly differs. Run 5 after cooling down with oxygen remains on a much lower level of conversion than Run 2. A possible explanation is, that the surface platinum oxide is first reduced very fast by NO at 150 °C. The conversion is hence at the same level as after cooling in the reaction gas mixture. Then above 200 °C the catalyst is reoxidised. The reoxidation is faster in the experiment after cooling down in oxygen, because perhaps more subsurface oxygen already exists. It might be that the subsurface oxygen was not reduced in the short time below 200 °C due to diffusion limitation.

3.1.3. NO temperature ramp with holding at minimal temperature

This experiment corresponds to the temperature ramp described in Section 3.1.1, but with an additional holding time at the minimal temperature. The experiment started after a reductive pretreatment with a repetition of Run 1 and 2 as described in Section 3.1.1. For comparison, Runs 1 and 2 are plotted in Fig. 6a–c. The temperature ramp was stopped at 160 °C (plot a), 180 °C (plot b) and 200 °C (plot c) for 1800 s with the following different atmospheres:

1 O2: 12% O_2 and 10% H_2O
2 O2+NO: 500 ppm NO, 12% O_2 and 10% H_2O
3 NO: 500 ppm NO and 10% H_2O

After holding at the minimal temperature, a rising temperature ramp followed to see the influence of this treatment on the NO conversion. In Fig. 6a, it can be seen that holding at 160 °C with 500 ppm NO without O_2 is increasing the NO conversion of the following temperature ramp significantly. It is nearly as good as Run 1, which followed the reductive pretreatment. So, in the absence of oxygen, NO is a very effective reductant for platinum oxide. On the contrary, holding with O_2 without NO is decreasing the activity in the following temperature ramp slightly, because further platinum oxidation takes place. Holding in the reaction gas mixture with O_2 and NO is slightly increasing the activity. This shows clearly that oxidation of platinum by O_2 and reduction of platinum oxide by NO are competing reactions. The same trend can be seen, if the minimal temperature of the ramp is raised to 180 °C, see Fig. 6b. The ramp called "0 s" corresponds to a rising temperature ramp which directly followed cooling down to 180 °C. It can be seen that the hysteresis is getting smaller compared to the temperature ramp until 160 °C, because at higher temperatures the oxidation of platinum prevails the reduction of PtO by NO. If oxygen is switched off while the 1800 s holding at 180 °C, reactivation takes place. If NO is switched off, the deactivation process goes on. Holding with the normal reaction gas mixture slightly increases the conversion compared to the ramp with no holding time. In Fig. 6c, the minimal temperature of the ramp was set to 200 °C. The hysteresis between cooling and rising temperature nearly disappears in the case with no holding time, because at 200 °C the reduction of platinum oxide is much slower than the oxidation of platinum. Holding with the reaction gas mixture or with oxygen hardly differs in activity. But holding with NO increases the activity significantly.

3.2. Isothermal experiments

Additionally to the experiments with temperature ramp, experiments with constant feed temperature have been undertaken to get
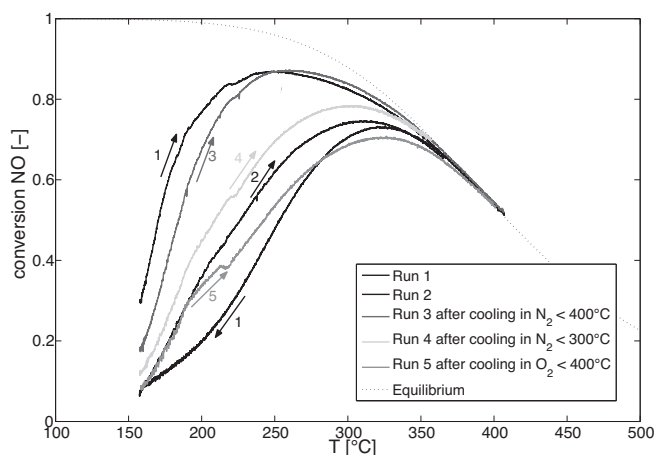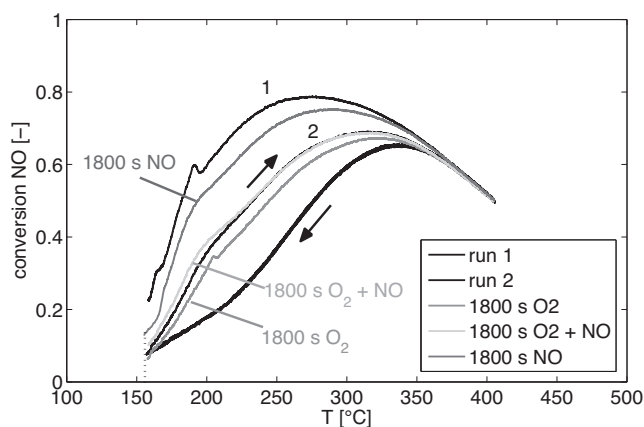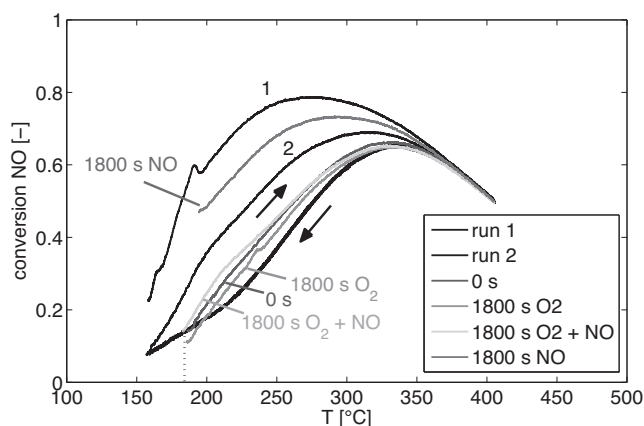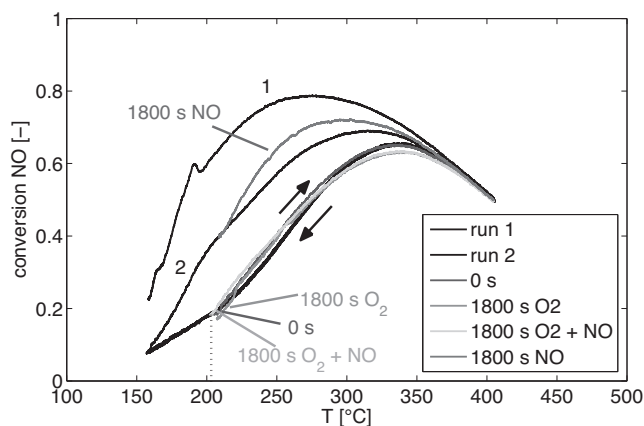
(a) holding at 160 °C

(a) Temporal progress at T=200 °C.

(b) holding at 180 °C

(b) Conversion of NO at the starting and after 3h for all temperature steps.

Fig. 7. NO oxidation measured for 3 h with 410 ppm NO, 100 ppm NO_2, 12% O_2, 7% CO_2 and 10% H_2O in the feed after pretreatment with 3% H_2 for 20 min.
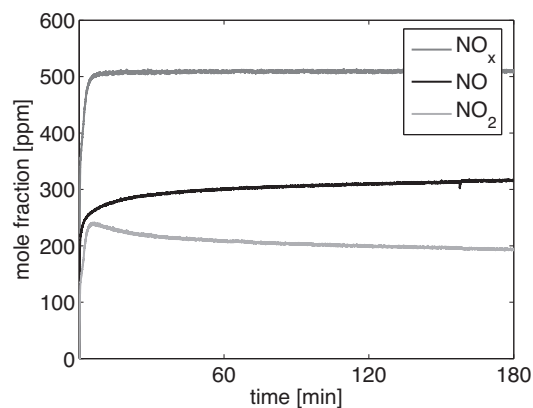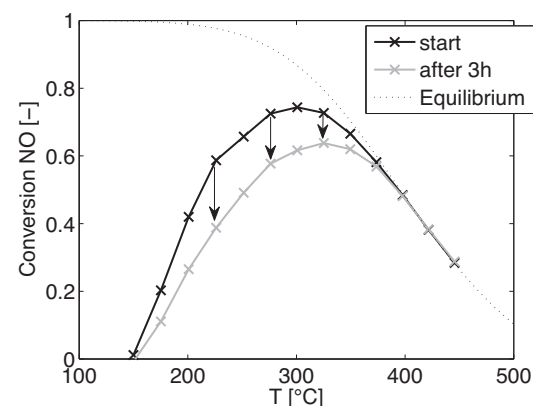

(c) holding at 200 °C

Fig. 6. NO oxidation (500 ppm NO, 12% O_2, 10% H_2O) measured while temperature ramp with holding at minimal temperature. "NO+O_2" refers holding in the normal reaction gas mixture. The holding called "O_2" is without 500 ppm NO in the feed and "NO" without 12% O_2. The temperature ramp called "0 s" corresponds to a rising ramp which directly follows cooling down.

information about the temporal progress of deactivation, similar to Olsson and Fridell [6,18]. The temporal progress of NO oxidation was measured for 270 and 510 ppm NO_x in the feed between 150 °C and 450 °C in intervals of 25 K. Before each experiment, the catalyst was pretreated with 3% H_2 for 20 min. For experiments below 350 °C, the temperature of the reducing pretreatment was

350 °C and the catalyst was cooled down in nitrogen afterwards. For experiments above 350 °C, the pretreatment took place at the same temperature as the experiment itself. In Fig. 7a, the progress of NO oxidation over three hours is shown at $T = 200$ °C with 410 ppm NO, 100 ppm NO_2, 12% O_2, 7% CO_2 and 10% H_2O in the feed. The NO concentration measured at the end of the reactor is increasing with time as the platinum is slowly oxidised by O_2 and NO_2 whereby the NO reaction rate is decreasing. At the end of the measurement after three hours, the NO conversion did not reach a stationary level. This shows the time scale in which the deactivation by platinum oxidation takes place.

The experiment was repeated between 150 °C and 450 °C in intervals of 25 K. As the catalyst was reduced before each temperature step, the conversion at the beginning of the experiment corresponds to the maximal conversion on pure platinum. In Fig. 7b, this conversion is plotted as "start" versus temperature for 510 ppm NO_x in the feed. The conversion at the end of the experiment is plotted as "after 3h". At 150 °C, the NO oxidation rate is so slow that no conversion of NO takes place, which does not change within the three hours. With increasing temperature, the conversion measured after three hours is clearly reduced compared to the conversion at the beginning of the experiment. Above 350 °C, the NO_2/NO ratio is thermodynamically limited, so that the platinum oxidation does not affect the NO conversion.

To evaluate the influence of the NO_2 content, deactivation was studied at 250 °C with an atmosphere of 12% O_2, 10% H_2O and 0/70/150 ppm NO_2 in the feed. The catalyst was pretreated at 350 °C
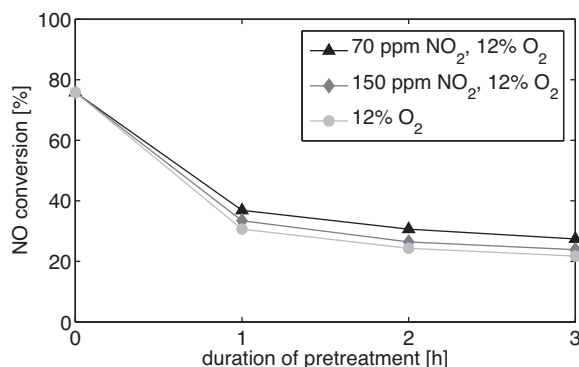
Fig. 8. Conversion of NO oxidation while deactivation with oxygen and with or without NO_2 at 250 °C.

with 3% H_2 for 20 min. At the beginning of the experiment and after each hour, the conversion of the NO oxidation was measured for five minutes with the following feed composition: 500 ppm NO, 12% O_2, 10% H_2O. It can be seen in Fig. 8 that during the first hour the conversion declines drastically. Thereafter the decrease is much smaller. In the presence of 12% O_2, the NO_2 content in the range of 70–150 ppm has nearly no influence on the deactivation.
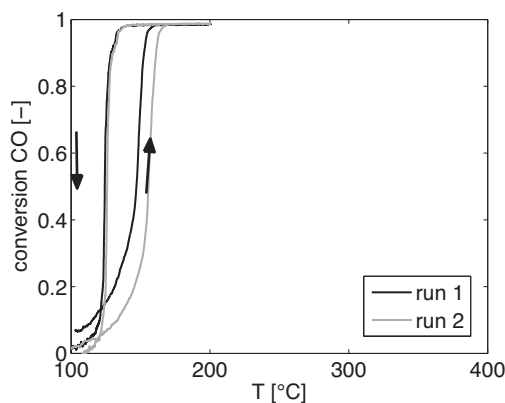
3.3. Mixture of CO and NO

3.3.1. CO temperature ramp

Before the experiment, the catalyst was pretreated with 3% H_2 at 350 °C for 1800 s. The first run of CO oxidation (2500 ppm CO, 12% O_2, 10% H_2O) already starts with a small conversion, which is increasing with rising temperature, see Fig. 9a. If the CO oxidation is examined without NO, the well-known hysteresis is observed, where the light-off occurs at higher temperatures than the light-out. Due to isothermal conditions in the flat bed reactor, there is no influence of heat release and the observed hysteresis can be completely attributed to surface coverage effects [28]. At the beginning of the experiment, the catalyst surface is covered with CO. Only if CO desorbs due to rise of temperature, empty adsorption sites arise, which enables oxygen to adsorb and the reaction to start. In contrast during light-out, the catalyst surface is already covered with oxygen, so that conversion can take place at lower temperature than during light-off. The second run has no conversion at low temperatures and the light-off temperature is 9 K higher as in the first run. We attribute this to platinum oxidation as well. As soon as CO is fully converted, the platinum surface is mainly covered with oxygen, by which platinum oxidation is promoted. Platinum oxide is less active for CO oxidation as the light-off takes place at a higher temperature in the second run.

3.3.2. CO and NO temperature ramp

In addition, the temperature ramp experiment was also investigated with a mixture of CO and NO after reductive pretreatment (3% H_2 at 350 °C for 1800 s). In the mixture with NO (500 ppm NO, 2500 ppm CO, 12% O_2, 10% H_2O), the CO light-off is shifted to higher temperature, which is caused by inhibition due to NO, compare Fig. 9b. As the repetition of the measurement (Run 2) had the same conversion like the measurement after reductive pretreatment (Run 1), only Run 2 is shown. Interestingly, the hysteresis of CO oxidation disappears. This is caused by the catalyst deactivation during the experiment, whereby the light-out occurs at a higher temperature. The measurements of Hauptmann et al. [1] even showed an inverse hysteresis for CO in a mixture with 430 ppm NO and 1000 ppm CO.

In the mixture with CO, the conversion of NO does not begin until 190 °C, which is the point when CO reaches full conversion

(a) 2500 ppm CO
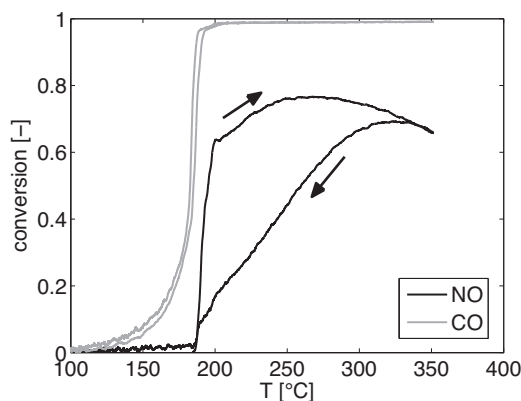
(b) 2500 ppm CO and 500 ppm NO

Fig. 9. Light-off and light-out for (a) pure CO and (b) a mixture of CO and NO under lean conditions (12% O_2, 10% H_2O).

(Fig. 9b). Before the platinum surface remains poisoned with CO which inhibits NO adsorption. After CO is converted, the NO conversion rises abruptly to 63%. This is a higher conversion than in the experiment without CO at the same temperature. The reason is, that the catalyst was poisoned with CO until that temperature. Due to this, neither O_2 nor NO_2 was adsorbed on the platinum surface, so no platinum oxidation occurs until the CO coverage decreases.

3.3.3. Isothermal CO oxidation

The catalyst was pretreated at 300 °C for 1200 s with 3% H_2 and 10% H_2O in N_2. Then it was cooled down in 10% H_2O in N_2 to 150 °C. The experiment started with a measurement of 120 s per each lateral withdrawal while 3000 ppm CO with 12% O_2, 7% CO_2 and 10% H_2O in N_2 were dosed. After the reaction had been going on for 1200 s, the measurement per each side was repeated. It can be seen from Fig. 10 that the reaction extinguishes within 20 min due to platinum oxidation. It has to be mentioned, that one lateral withdrawal is measured after another so that deactivation already takes place while measuring the initial conversion profile named "0 s".

Compared with the CO oxidation in Fig. 9a, it can be seen that 150 °C is exactly in the light-off temperature range where a high conversion is reached in the first run but a low conversion in the second run. So the isothermal experiment confirms the finding of the light-off experiments that platinum oxidation also takes place during CO oxidation due to the very lean conditions with 12% oxygen in the gas atmosphere.
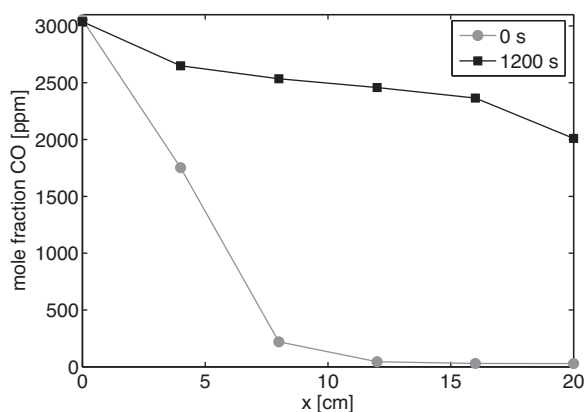
Fig. 10. Axial profiles along the catalyst length of CO oxidation at 150 °C with 3000 ppm CO, 12% O_2, 7% CO_2 and 10% H_2O in N_2 at the beginning of the experiment and after 1200 s.

3.4. H_2-titration

With the experiments presented in Section 3.1 and 3.2, the impact of the platinum oxidation on the NO oxidation can be measured but not the platinum oxide fraction itself. Olsson and Fridell et al. [6,18] used XPS analysis to measure the relative abundance of Pt, PtO and PtO_2 for a Pt/BaO/Al_2O_3-NSC and a Pt/Al_2O_3-DOC after pretreatment with H_2, NO_2 and O_2. Yoshida et al. [29] showed that a quantitative determination of the oxygen to platinum ratio is possible by O_2-TPD, temperature programmed desorption of oxygen. In the following, a temperature programmed reduction is applied for determination of the platinum oxide fraction.

A H_2O peak was observed, when the catalyst was reduced after NO oxidation with H_2, due to the reaction of the hydrogen with

Table 1
Overview of the duration of NO oxidation before reduction with H_2 for the titration experiments.

Run	Duration (min)
1	5
2	10
3	20
4	30
5	60
6	120
7	180
8	240
9	300

the oxygen stored as platinum oxide. We considered if the platinum oxide fraction can be determined by the area of the H_2O peak. Therefore a H_2-titration was conducted, for which the duration of the preceding NO oxidation was varied between 300 s and 5 h, see Table 1. The experiment was run at 200 and 250 °C. For better measurability of the H_2O peak, no water was dosed. The feed during NO oxidation consisted of 405 ppm NO, 105 ppm NO_2 and 12% O_2. After NO oxidation, the catalyst was flushed with nitrogen for 120 s. Then, the regeneration with 3% H_2 in N_2 followed with a duration of 30 min. Additionally, the catalyst was heated up to 350 °C during the regeneration. Afterwards, the catalyst was cooled down in inert atmosphere.

As shown in Fig. 11c, a noticeable H_2O peak develops when the feed gas is switched to regeneration conditions. Furthermore, a peak of NO and NO_2 is observed, which is plotted summarized as NO_x in Fig. 11a. In addition to water and NO_x, ammonia is also formed, see Fig. 11b.

By integration, the molar amount of desorbed component is calculated, which is plotted in Figs. 12 and 13 for the respective
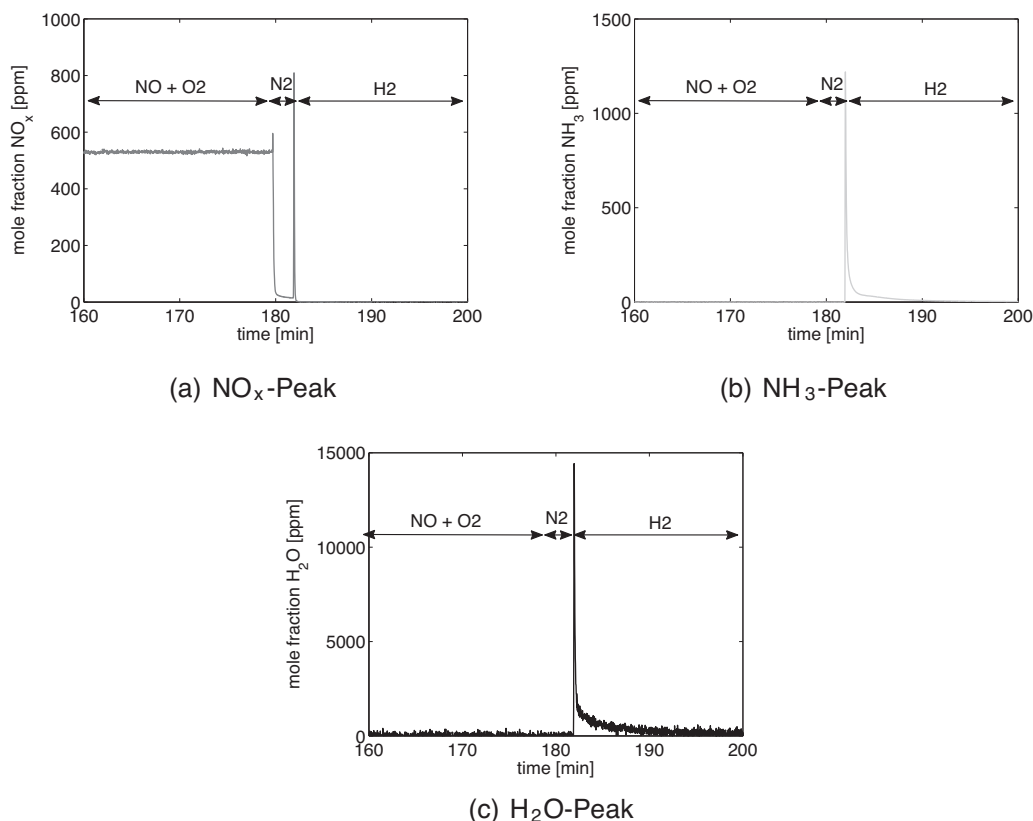

(a) NO_x-Peak

(b) NH_3-Peak

(c) H_2O-Peak

Fig. 11. Desorption peaks at 250 °C for a preceding three hours lasting NO oxidation.
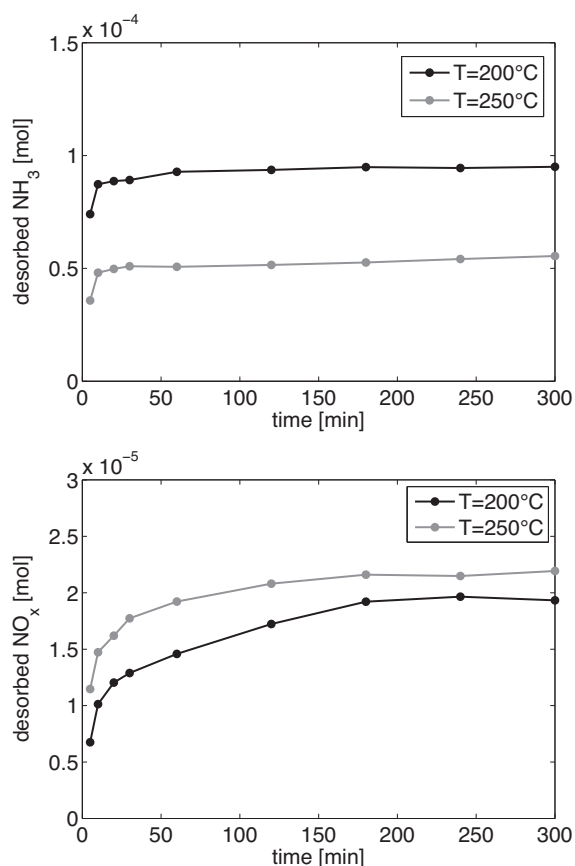
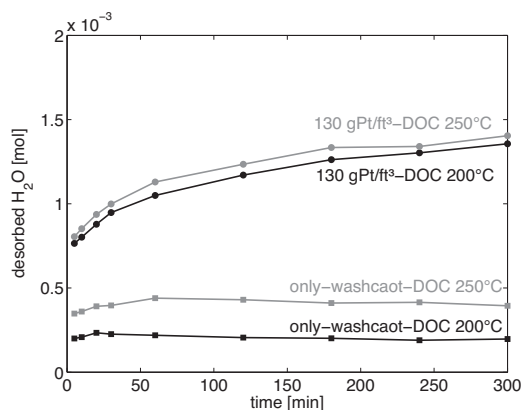**Fig. 12.** Amount of desorbed NH_3/NO_x versus duration of preceding NO oxidation.

Fig. 13. Amount of desorbed H_2O while H_2-regeneration versus duration of preceding NO oxidation for a washcoat-only-DOC and platinum loaded DOC.

components versus the duration of the preceding NO oxidation which can be considered as an oxygen storage time.

It can be seen, that the amount of desorbed NO_x is in the magnitude of platinum surface sites, see Table 2. Therefore, it can be assumed, that the desorbed NO_x was adsorbed on the

Table 2
Theoretical number of mol platinum at the surface of the platinum particles and total number of platinum atoms on the five catalyst slices used in the flat bed reactor. The number of accessible platinum atoms was determined by chemisorption measurements at ITCP, University Karlsruhe [27].

Pt (total)	(mol)	$1.8 \cdot 10^{-4}$
Pt (surface)	(mol)	$2.0 \cdot 10^{-5}$

platinum/platinum oxide surface. Surprisingly, the desorbed amount is higher at 250 °C than at 200 °C. By pure adsorption, less NO_x would be adsorbed at higher temperatures. So NO_x adsorbs not only on the platinum surface but perhaps formed a compound with the aluminia oxide of the washcoat.

The amount of desorbed NH_3 is constant over storage time, so it can be concluded that ammonia does not evolve related to the oxygen storage at platinum oxide.

The H_2O peak is increasing with rising duration of the preceding NO oxidation for the catalyst with platinum while it is constant for the catalyst without platinum, see Fig. 13. Thus, the increase can be clearly related to the oxygen storage effect during platinum oxidation. For short durations, a fast increase is noted, because first the easily accessible platinum surface will be oxidised. The deeper the platinum oxidation progresses in the platinum bulk phase, the slower it proceeds. Even after five hours no stationary level is reached, which is in accord with the duration of deactivation reported in literature [8,1] and the measurements in Section 3.2.

According to Table 2, in the worst case, if all platinum atoms were oxidised to PtO_2, the maximum H_2O amount which could evolve is $3.6 \cdot 10^{-4}$ mol. The measured amount of H_2O is at least one order of magnitude higher, see Fig. 13. This means, that additional oxygen was adsorbed at the washcoat, which reacts with H_2 during regeneration. As the washcoat-only-DOC without platinum was produced several years before, it has not the same washcoat composition and surface area. For this reason a quantitative determination of platinum oxide is not possible from these measurements. But it could be seen clearly, that the platinum oxide fraction is increasing with the duration of the preceding NO oxidation.

4. Discussion

In the experiments presented in Section 2, the oxidising agents O_2 and NO_2 are present. According to Olsson and Fridell [6], who analysed a similar catalyst (Pt/Al_2O_3-DOC) by XPS, the species Pt, PtO and PtO_2 are found after oxidising pretreatment with O_2 or NO_2. Consequently, platinum could be oxidised by the reactions Eqs. 1–4.

$$Pt + 0.5O_2 \leftrightarrow PtO \tag{1}$$

$$PtO + O_2 \leftrightarrow PtO_2 \tag{2}$$

$$Pt + 0.5NO_2 \leftrightarrow PtO + NO \tag{3}$$

$$PtO + NO_2 \leftrightarrow PtO_2 + NO \tag{4}$$

From the experimental data it can be concluded that:

- Platinum oxidation is a slow process which takes place in the range of minutes and hours.
- Above 350 °C, platinum oxide decomposes to platinum due to thermal decay. Therefore, reactions 1 and 2 have to be specified as equilibrium reactions.
- Platinum oxide is reduced at low temperatures by NO. Hence, reactions 3 and 4 have to be reversible.
- In presence of 12% O_2, 150 ppm NO_2 have no influence on the progress of platinum oxidation, see Section 3.2.
- Oxidation of platinum by O_2 and reduction of platinum oxide by NO are competing reactions. The oxidation of platinum is slower at low temperatures but with rising temperature it is getting faster than the reduction of platinum oxide.
- There is no indication that a distinction between PtO and PtO_2 is necessary. In the following only PtO is considered as oxidised species.
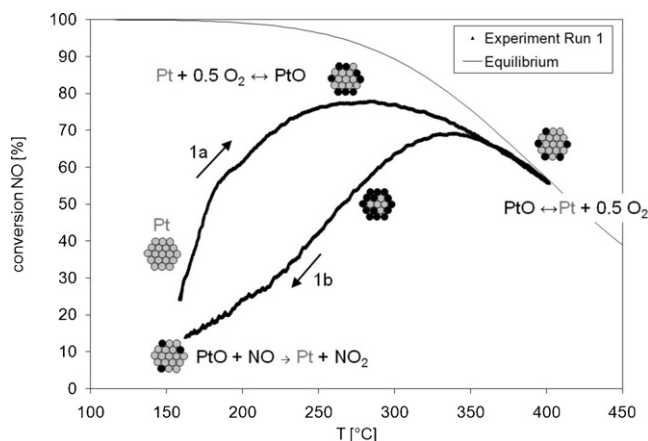
Fig. 14. First run of NO oxidation (500 ppm NO, 12% O_2, 10% H_2O) directly after reducing pretreatment with 3% H_2 with linear temperature ramp (±5 K/min). (1a) Heating, (1b) cooling.

The temperature ramp shown in Fig. 3 can then be explained by the scheme depicted in Figs. 14 and 15. At the beginning of Run 1a pure platinum is present, which is then progressively oxidised by O_2. Above 350 °C, platinum oxide decomposes due to thermodynamic equilibrium limitation. When cooling down (Run 1b), platinum oxide is formed again. At low temperatures, a part of the platinum oxide is reduced by NO, which is not as effective as the reduction by H_2, so that Run 2a shows less activity than after H_2 pretreatment.

The different activity after cooling (compare Section 3.1.2) can be explained by this concept as well. If the catalyst is cooled down in nitrogen, the platinum cannot be further oxidised and the platinum content will be frozen on the previous level. As platinum oxide thermally decays at higher temperatures, less platinum oxide will be present at 400 °C than at 300 °C and therefore after cooling in nitrogen the activity will be higher. If cooled down with 12% O_2, platinum is reoxidised while cooling down and is therefore less active in the following rising temperature ramp.

Based upon these observations, a simulation modell is presently under development, results of which will be presented in a subsequent publication.
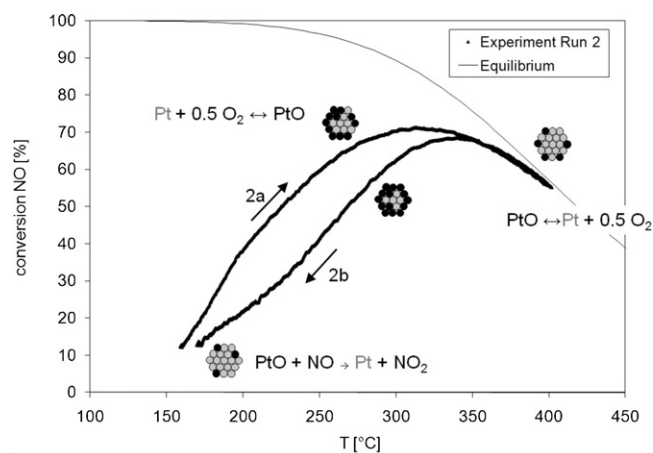

Fig. 15. Second run of NO oxidation (500 ppm NO, 12% O_2, 10% H_2O) directly after the first run without any pretreatment with linear temperature ramp (±5 K/min). (2a) Heating, (2b) cooling.

5. Conclusions

Deactivation effects due to platinum oxidation of near series Pt-Al_2O_3 DOC were studied in an isothermal flat bed reactor. The experiments showed that platinum oxidation is a slow process in the time range from minutes to hours. If there is excess oxygen like in diesel exhaust gas, a NO_2 content in the range of <200 ppm has no effect as additional oxidant for platinum. In contrast, the NO plays a critical role as it is able to reduce platinum oxide below 220 °C even in the presence of oxygen, which causes a reactivation of the catalyst. At temperatures above 350 °C, platinum oxide is decomposed to platinum due to thermodynamical limitation. The oxidation of platinum in the mid-temperature range in combination with the reduction of platinum oxide in the low temperature range respectively the thermal decay in the high temperature range is causing a hysteresis in NO conversion if the temperature is varied at constant gas atmosphere. Platinum oxidation is also observed during CO oxidation after reductive pretreatment due to the oxygen-rich gas atmosphere. The light-off and light-out behaviour of CO and NO in a mixture of both components is strongly influenced by each another. H_2-titration experiments prove that indeed more oxygen is stored as platinum oxide with increasing duration of NO oxidation although a quantification of the amount of Pt oxide is impossible because of the simultaneous reduction of other catalyst components.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2012.04.008.

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